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Ionic Liquid Polymer Electrolyte Based on Bis(fluorosulfonyl)Amide for Sodium Secondary Batteries

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A new ionic liquid polymer electrolyte (ILPE) has been prepared for sodium secondary batteries. The ILPE is prepared by using a cast technique in which poly(vinyl chloride) used as a host polymer. The ILPE shows an ionic conductivity of 5.6 mS cm⁻¹ at 318 K with 50 wt% of bis(fluorosulfonyl)amide ionic liquid. The stability of the ILPE reached 473 K based on 5 wt% loss. Sodium metal electrodeposition/dissolution was observed at the cathodic limit of the electrochemical window.

Introduction

Lithium secondary battery is used in various applications such as in portable electronics, daily use devices and auto motive [1, 2]. In addition, the growing demand for lithium-containing chemicals might limit the application of lithium secondary batteries in large scale energy storage system. This has resultant awareness to discover alternative energy devices.

Sodium secondary battery turns out to be one of the most potential alternatives due to abundant sodium resources [3]. The key properties for the use of sodium-based technology as alternative energy storage device are its high abundance, low cost and low redox potential ($E^{\circ}_{\text{Na}^+/\text{Na}} = -2.71$ vs SHE; 0.3 V above that for $E^{\circ}_{\text{Li}^+/\text{Li}}$).

Organic electrolytes are currently used in many researches in Na secondary batteries [4, 5] whereas the use of ionic liquids offers great advantages such as low vapour pressure, low-flammable, high thermal stability, high conductivity and wide electrochemical window, making them serious contenders for safer batteries [6, 7]. Physical and electrochemical properties of ionic liquids specifically for Na secondary batteries were studied in recent works [8-12]. Although ionic liquids provide great advantages, they cannot stand alone; polymerization is one of the important techniques in real application in order to retain the value of ionic liquids and avoid leakage.

The “ionic liquid polymer electrolytes (ILPE)” can be classified into “gel polymer electrolytes (GPE)” and consist of ionic liquids, host polymer and other component for electrochemical reactions. In ILPE, it is assumed that the ionic liquid phase is trapped within polymer matrix forming a self-standing polymer electrolyte with the ions moving in the liquid phase. The advantages of ILPE are high processability, high flexibility, low cost, and high dimensional stability that could lead to the elimination of the separator. In comparison with conventional separator, ILPE offers a better electrolyte trapping capability of liquid electrolytes [13] and acts as a separator and electrolyte at the same time.

One of the most challenging features in this area is improvement of the compatibility between the ionic liquid, salt and host polymer. For sodium ion conducting ILPE, only a few kinds of polymer have been demonstrated as a host polymer which are poly(vinylidene di- fluoride-co-hexafluoropropylene, P(VdF-HFP))[14], poly(vinylidene difluoride), (PVdF) and Poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP)[15].

From the fundamental point of view, weaker interaction of Na^+ with the host polymer and weaker ion-ion interaction compared to that of Li^+ -based polymer electrolyte may result in more efficient creation and transport of Na^+ charge carrier. [16]

In this work, we prepared ILPE for Na^+ secondary battery based on $\text{Na}[\text{FSA}]$ (FSA^- = bis(fluorosulfonyl)amide), $[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ ($\text{C}_2\text{C}_1\text{im}^+$ = 1-ethyl-3-methylimidazolium) and poly(vinyl) chloride (PVC). The conductivity, thermal stability and electrochemical behavior of ILPE will be discussed.

Experimental

Materials

Air sensitive materials were handled in a glovebox under a dried and deoxygenated argon atmosphere. The $\text{Na}[\text{FSA}]$ salts and $[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ ionic liquid were purchased and vacuum-dried at 353 K prior to use. PVC analytic standard (average M_w 85,000, Fluka) was used as received.

Preparation of gel polymer electrolyte

The ILPE films were prepared by a solution casting technique. One gram of PVC was dissolved in 40 mL tetrahydrofuran (THF) and the mixture was stirred vigorously until clear homogenous solution was formed. The two salts, $[\text{C}_2\text{C}_1\text{im}][\text{FSA}]$ and $\text{Na}[\text{FSA}]$, were added in appropriate ratios into the solution and stirred for 24 hours until a transparent and homogenous solution formed. This process was carried out at room temperature. The viscous solution was cast into petri dish and left in open air to allow the evaporation of THF. The film was then dried under vacuum at 333 K for 48 hours. Finally, the flexible and

self-standing polymer electrolyte was formed. All the films were stored in the glove box. Table 1 indicates the composition of the $[\text{C}_2\text{C}_{1\text{im}}][\text{FSA}]\text{-Na}[\text{FSA}]\text{-PVC}$ ILPE films prepared in the present study.

TABLE I: Composition of $[\text{C}_2\text{C}_{1\text{im}}][\text{FSA}]\text{Na}[\text{FSA}]\text{-PVC}$ polymer electrolyte

No	Code name	Weight ratio			Fraction of $[\text{C}_2\text{C}_{1\text{im}}][\text{FSA}]$ (wt%)
		$[\text{C}_2\text{C}_{1\text{im}}][\text{FSA}]$	$\text{Na}[\text{FSA}]$	PVC	
1	ILPE-1	0	1.0	1.0	0
2	ILPE-2	0.5	1.0	1.0	20.0
3	ILPE-3	1.0	1.0	1.0	33.3
4	ILPE-4	1.5	1.0	1.0	42.9
5	ILPE-5	2.0	1.0	1.0	50.0

Analysis

Ionic conductivity of the ILPE was measured by impedance analyzer (3520-80, Hioki E.E. Corp). The ILPE was placed between a pair of stainless steel blocking electrodes. The data were collected between 4.0 to 1.0×10^6 Hz with the amplitude of 10 mV at the open circuit potential. Thermal analysis of the ILPE was performed on a Netzsch TG (thermogravimetric analysis, STA409EP) from 308 K to 823 K under dry nitrogen at a heating rate 5 K min^{-1} . Cyclic voltammetry was performed in a two-electrode cell (2032 coin cell) with Cu working and Na counter electrodes.

Results and discussion

Ionic Conductivity

Figure 1 shows the ionic conductivities of ILPEs versus the weight fraction of $[\text{C}_2\text{C}_{1\text{im}}][\text{FSA}]$ ionic liquid at 318 K. The ionic conductivity increases with increasing the amount of ionic liquid. This trend is in a good agreement with the previous study for ILPE containing N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide $[\text{C}_4\text{C}_{1\text{pyrr}}][\text{NTf}_2]$ for lithium ion batteries [17]. The ILPE-1 shows the lowest conductivity of $5.26 \times 10^{-9} \text{ S cm}^{-1}$, suggesting this system does not work without ionic liquid. The ILPE-5 with 50% of ionic liquid gives the highest ionic conductivity ($5.63 \times 10^{-3} \text{ S cm}^{-1}$) in this series. Addition of the ionic liquid weakens the interaction between the polymer chain and hence enhance diffusion of ions in the matrix.

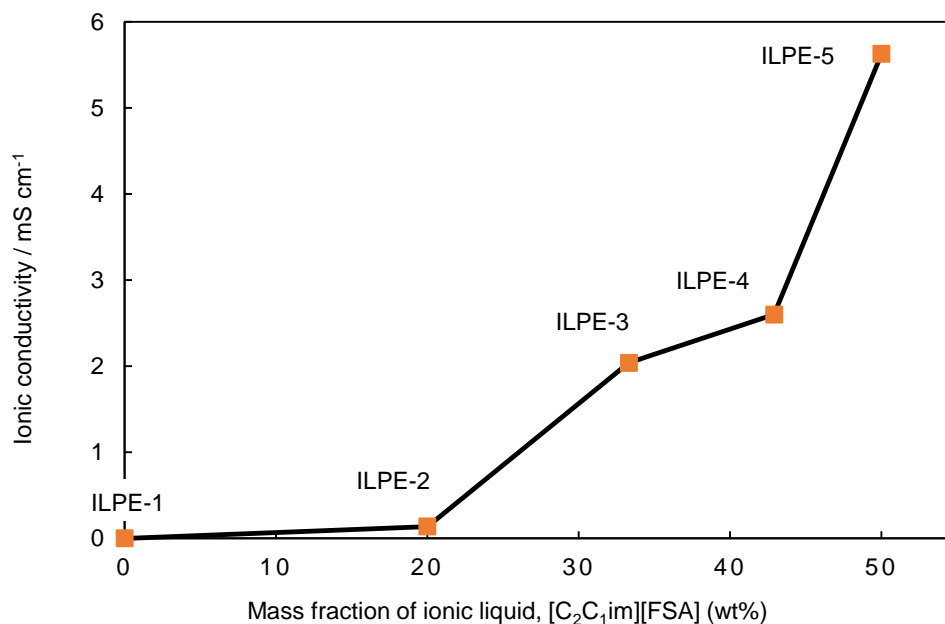


Figure 1. Ionic conductivity of the ILPEs at 318 K

Thermal Stability

Figure 2 shows thermogravimetric curves for the ILPE-5, neat PVC polymer and [C₂C₁im][FSA] ionic liquid. The decomposition temperature of the ILPE reached 473 K based on the 5 wt% loss under this condition. It suggests that the stability of the host polymer, PVC, plays an important role to determine the thermal stability of the ILPE since the stability of the ionic liquid used in this study is higher in comparison with the host polymer.

Electrochemical behavior

It was reported for the Na[FSA]-[C₂C₁im][FSA] ionic liquid system that Na metal deposition/dissolution occurs at the cathodic limit [10]. In this experiment, ILPE-5 was selected because of the highest conductivity among the ILPEs prepared in the present study. Figure 3 indicates that the Na metal deposition/dissolution occurs for ILPE-5 with the coulombic efficiency of 57.4%. It should be noted this electrochemical reaction occurs around -0.1 vs Na metal in the present condition, suggesting that the Na metal counter electrode is working as a quasi-reference electrode and does not indicate the potential of the standard Na⁺/Na redox couple. Similar behavior was observed for the gelled ionic liquid sodium ion conductors for sodium batteries [18]. The deposition overpotential observed in the Na[FSA]-[C₂C₁im][FSA] ionic liquid was not observed for this ILPE suggesting that the interfacial process is smoother in the solid state in comparison with that in the liquid state [12].

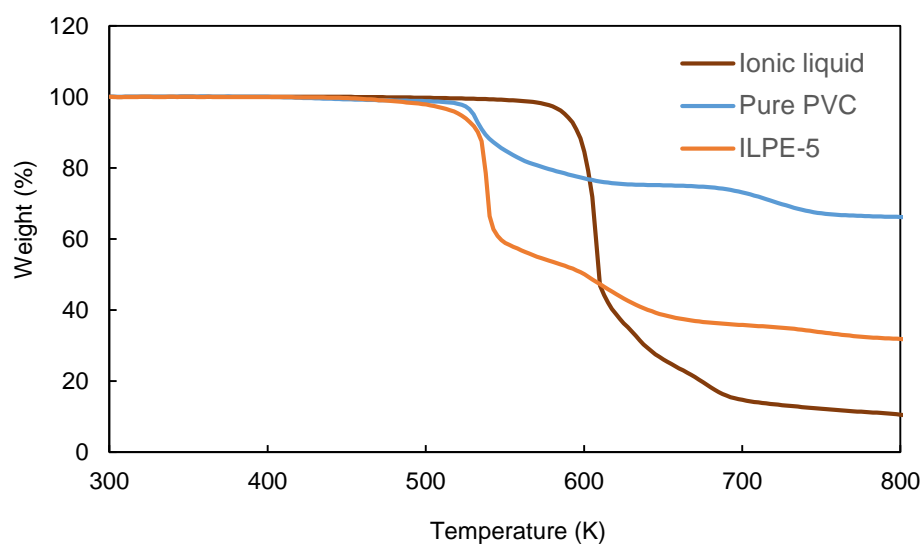


Figure 2. Decomposition temperature of ILPE-5, PVC polymer and $[C_2C_1im][FSA]$ ionic liquid.

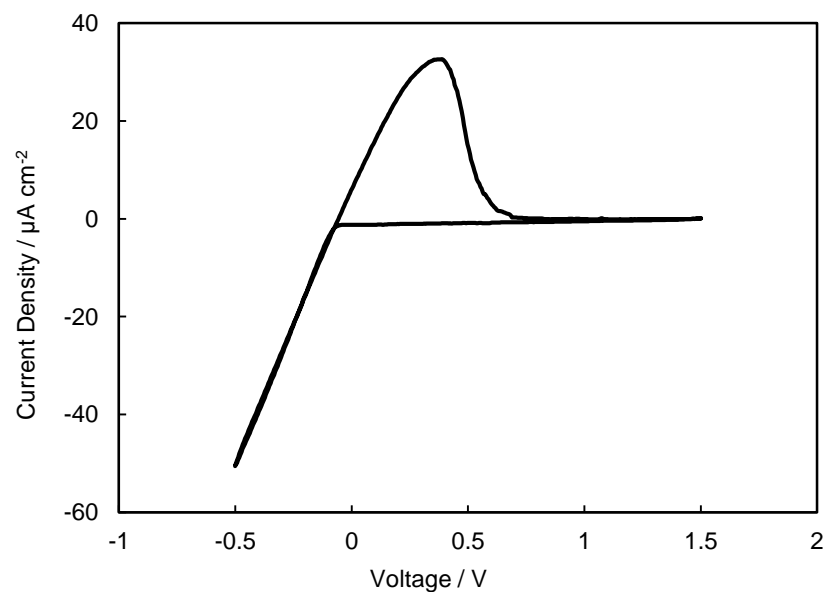


Figure 3. Cyclic voltammogram of ILPE-5 in a two electrode cell. The working and counter electrodes are Cu and Na plates, respectively.

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